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A XANTHONE FROM PERICARPS OF *GARCINIA MANGOSTANA*

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Key Word Index—*Garcinia mangostana*; Guttiferae; pericarp; mangostinone; α-mangostin; β-mangostin; γ-mangostin; gartanin; garcinone E; 1,5-dihydroxy-2-(3-methylbut-2-enyl)-3-methoxyxanthone; 1,7-dihydroxy-2-(3-methylbut-2-enyl)-3-methoxyxanthone.

Abstract—A new xanthone with a geranyl group, mangostinone, was isolated from pericarps of *Garcinia mangostana*, in addition to seven known xanthones, α-, β- and γ-mangostins, gartanin, garcinone E, 1,5-dihydroxy-2-(3-methylbut-2-enyl)-3-methoxy- and 1,7-dihydroxy-2-(3-methylbut-2-enyl)-3-methoxyxanthone. The structures were determined by means of spectroscopic analysis.

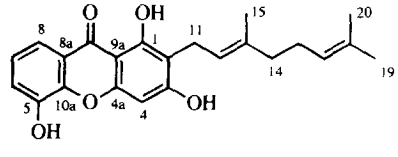
INTRODUCTION

The chemical constituents of *Garcinia subelliptica* [1–3] and *Calophyllum inophyllum* [4–6] were dealt with in our previous papers. In continuation of our study oriented to search for xanthone derivatives with bioactive potency in guttiferous plants, we examined chemical constituents in pericarps of *G. mangostana*. In this paper, the isolation and characterization of a new xanthone and seven known xanthones is described.

RESULTS AND DISCUSSION

Pericarps of *G. mangostana* collected in Bali, Indonesia, were dried and ground, and extracted with *n*-hexane, benzene, acetone and 70% MeOH, successively. The benzene extract was concentrated and dissolved in MeOH to afford crude crystals mainly composed of α-mangostin. The crystals were filtered off and the filtrate chromatographed on silica gel and Sephadex LH-20 to give eight xanthones (**1**–**8**).

Compound **1**, mangostinone, obtained as a yellow amorphous powder, reacted positively with Gibb's and $FeCl_3$ reactions. The $[M]^+$ at *m/z* 380.1601 in the HREI-mass spectrum corresponds to the empirical formula $C_{23}H_{24}O_5$ (calc. 380.1623). The UV spectrum suggested that **1** was a xanthone derivative. In the ^1H NMR spectrum, an aromatic proton (δ6.57) and protons based on a 1,2,3-trisubstituted benzene ring [δ7.26 (1H, *t*, *J* = 7.8 Hz), 7.32 and 7.68 (1H each, *dd*, *J* = 7.8, 1.5 Hz)], as well as a chelated (δ13.25) and two phenolic hydroxyl groups (δ9.15 and 9.70), were observed. The spectrum further showed the presence of a C_{10} alkyl chain [δ1.55, 1.60 and 1,81 (3H each, *s*, Me × 3), 1.98 (4H, *m*), 3.39 (2H, *d*, *J* = 6.8 Hz), 5.08 and 5.31 (1H each, *t*-like *m*)]. In the ^{13}C NMR spectrum, three methyl groups of the C_{10} unit were exhibited at δ16.3, 17.7 and 25.8, indicating that the C_{10} unit was a geranyl chain. In the HMBC spectrum (Fig. 1), the chelated hydroxyl group was correlated to three quaternary aromatic carbons (δ103.8, 111.7 and 161.7), the latter two of which were further correlated to the methylene protons (δ3.39) of the geranyl chain. Two aromatic carbons (δ103.8 and 111.7) which had cross-peaks to the chelated hydroxyl group were also correlated to the aromatic proton (δ6.57). Therefore, **1** was a 2-geranyl-1,3-dihydroxyxanthone. This tentative partial structure was confirmed by other correlations in the HMBC spectrum. The position of the remaining free hydroxyl group was determined as follows. In the HMBC spectrum (Fig. 1), one of the aromatic protons (δ7.68) in the 1,2,3-trisubstituted benzene ring caused a cross-peak to the carbonyl carbon, which indicated that the partial structure in another benzene ring was 5-hydroxyxanthone. In the ^{13}C NMR spectrum, the chemical shifts of the quaternary aromatic carbons with an O-function



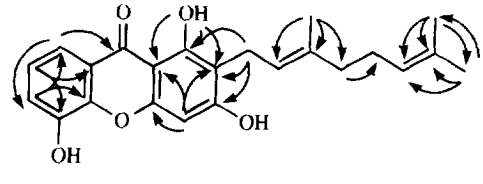


Fig. 1. HMBC (*J* = 10 Hz) spectrum of **1**.

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were found at δ146.1 and 146.9, which substantiated that the partial structure of **1** was 5-hydroxyxanthone. Thus, the structure of mangostinone was characterized as **1** (2-geranyl-1,3,5-trihydroxyxanthone).

Compounds **2**–**8** were identified by spectral analysis as α- (**2**), β- (**3**) and γ-mangostin (**4**), gartanin (**5**), garcinone E (**6**), 1,5-dihydroxyl-2-(3-methylbut-2-enyl)-3-methoxy- (**7**) and 1,7-dihydroxy-2-(3-methylbut-2-enyl)-3-methoxy-xanthone (**8**), respectively.

Although many xanthones alkylated with C_5 unit(s) have been isolated from *G. mangostana* [7, 8], this is the first isolation of a xanthone with a C_{10} unit from this species.

EXPERIMENTAL

Plant material. Pericarps of *G. mangostana* L. were collected in Bali, Indonesia, in April 1993. Voucher specimens are deposited in the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation. Dried and ground pericarps (2.7 kg) were extracted in *n*-hexane (5 l × 3), benzene (5 l × 3), Me_2CO (5 l × 3) and 70% MeOH (5 l × 3), successively, under reflux. The benzene extract (30 g) was recrystallized from MeOH to give crude, amorphous α-mangostin. The residue (8 g) was chromatographed on silica gel CC eluted with a *n*-hexane–EtOAc system. The *n*-hexane–EtOAc (3:1) eluate was further subjected to silica gel vacuum liquid chromatography (VLC) eluted with the same system and finally purified by Sephadex LH-20 CC, eluting with MeOH to give **1** (5 mg).

Compound **1** (*mangostinone*). Yellow amorphous. HREI-MS: *m/z* 380.1601 for $C_{23}H_{24}O_5$ (calc. 380.1623). EIMS *m/z* (rel. int.): 380 $[M]^+$ (23), 311 (65), 295 (21), 269 (22), 257 (100), 229 (9), 228 (8), 137 (7), 69 (53), 41 (51). UV λ (MeOH) nm: 244, 250sh, 318, 345sh; + NaOMe: 212, 242sh, 280sh, 357. ^{1}H NMR (400 MHz, acetone-d_6): δ1.55 (3H, *s*, H-20), 1.60 (3H, *s*, H-19), 1.81 (3H, *s*, H-14), 1.98 (4H, *m*, H-14, H-16), 3,39 (2H, *d*, J = 6.8 Hz, H-11), 5.08 (1H, *t*-like *m*, H-17), 5.31 (1H, *t*-like *m*, H-12), 6.57 (1H, *s*, H-4), 7.26 (1H, *t*, J = 7.8 Hz, H-7), 7.32 (1H, *dd*, J = 7.8, 1.5 Hz, H-6), 7.68 (1H, *dd*, J = 7.8, 1.5 Hz, H-8), 9.15, 9.70 (1H each, *br s*, OH × 2), 13.25 (1H, *s*, C-1-OH). ^{13}C NMR (100 MHz, acetone-d_6): δ16.3 (C-15), 17.7 (C-20), 22.0 (C-11), 25.8 (C-19), 27.5 (C-16), 40.6 (C-14), 94.4 (C-4), 103.8 (C-9a), 111.7 (C-2), 116.5 (C-8), 121.3 (C-6), 122.4 (C-8a), 123.3 (C-12), 124.8 (C-7), 125.1 (C-17), 131.7 (C-18), 135.5 (C-13), 146.1 (C-10a), 146.9 (C-5), 156.5 (C-4a), 161.7 (C-1), 164.1 (C-3), 181.7 (C-9).

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